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16. ABSTRACT

This study was conducted to investigate the effects of deposition on galvanized steel and painted panels using mobile covering/deionized spray devices at exposure sites located at Steubenville, OH and Research Triangle Park (RTP), NC. Ambient rain and deionized spray runoff samples from the panels were collected on an event basis for seven months and under went detailed chemical analysis. The analysis indicated that the dry deposition of acid gases at the sites increased the dissolution rate of galvanized steel corrosion products. Although the average SO_2 level in Steubenville was ten times the RTP value, the rate of Zn dissolution was only 1.9. This result in conjunction with the presence of large amounts of Ca in the Steubenville runoff samples suggest that neutralization of acidic gases by dry deposited basic particulates may be important at the Steubenville site. At the RTP site low levels of anions were found in the runoff from the painted panel with H^+ as the most abundant cation. This result is consistent with the lack of reactivity towards acidic gases due to the absence of alkaline paint components.

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ATMOSPHERIC WEATHERING CAUSED BY DRY DEPOSITION OF ACIDIC COMPOUNDS

Key Words: atmospheric weathering, corrosion, dry deposition, galvanized steel, oil-based paint, acid deposition, neutralization.

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ABSTRACT

Controlled field studies were conducted at material exposure sites at Research Triangle Park, NC, and Steubenville, OH, between April 25, 1987, and December 28, 1987. Automatic covering/spray systems located at each site were used to expose panels of galvanized steel and paints under the following conditions: (1) dry deposition only, (2) dry plus ambient wet deposition; and (3) dry deposition plus deionized water (DI). Ambient and DI-runoff samples were collected on an event basis and underwent detailed chemical analyses. The results from the analyses of the DI-runoff samples from galvanized steel and oil-based paint panels from each site are presented in this paper. The runoff results show that the dry deposition of acid gases at the sites increased the dissolution rate of galvanized steel corrosion products. At

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the Ohio site, gases and particulates leading to the formation of $SO_4^=$ in the DI-runoff were the major contributing species to the dissolution rate. At the North Carolina site, this preliminary analysis suggests that in addition to $SO_4^=$, precursors to runoff NO_3^- and $HCOO^-$ may contribute to the Zn dissolution rate. Although the average SO_2 level in Steubenville was 10 times the North Carolina value, the Ohio to North Carolina Zn dissolution rate was only 1.9. This result, in conjunction with the presence of large amounts of dry-deposited Ca in the Ohio runoff samples, suggests that the neutralization of acid gases by dry-deposited basic particulates may have been important at the Ohio site. At the North Carolina site, low levels of anions were found in the paint runoff with H^+ as the most abundant cation, a result consistent with the anticipated lack of reactivity toward acid gases due to the absence of alkaline-paint components. The presence of large runoff concentrations of Ca and $SO_4^=$ at the Ohio site can be explained by increased reactivity of the surface due to dry-deposited basic particles and/or dry deposition of $CaSO_4$.

INTRODUCTION

Outdoor materials degrade by natural-weathering processes and by reactions with air pollutants. Natural-weathering processes include interactions involving moisture, heat, oxygen, ultraviolet radiation, and various bacteria and fungi. Pollution-induced damage is initiated by dry deposition of gas- and aerosol-phase pollutants and wet-deposited impurities in precipitation. Sensitive materials include materials of construction such as paints and metals and those of cultural significance including decorative pieces, statues, and monuments. Although many degradation modes have been studied qualitatively (1,2), only recently has an effort been undertaken to develop models for predicting atmospheric weathering rates. Much of this work is conducted under the National Acid Precipitation Assessment Program (NAPAP) Effects on Materials Task, whose goal is to develop models for determining the economic savings of a particular control strategy (3).

As part of this program we have designed and initiated controlled field studies capable of separating the damaging effects of dry and wet deposition to materials (4,5). Automated covering/spray systems are used to expose materials under the following conditions: (1) dry deposition only; (2) dry plus ambient wet deposition;

and (3) dry deposition plus deionized water (DI). Under the third condition, test panels are protected from ambient precipitation during an event and are sprayed with an amount of DI approximately equal to the volume of precipitation. Exposure systems are located in Research Triangle Park, NC, a relatively unpolluted site, and Steubenville, OH, a site with high levels of SO_2. Runoff collectors are mounted at some of the test-panel positions and are used to collect ambient rain and DI-runoff samples. Samples are collected on an event basis and undergo detailed chemical analysis.

Recently we reported results of the runoff analyses obtained from test panels of galvanized steel and paints at the North Carolina site (4,5), showing that the dry and wet deposition of acidic compounds enhance the dissolution rates of galvanized steel corrosion products and certain basic components of paint films such as $CaCO_3$ and ZnO. To expand on these findings, here we report results of runoff experiments conducted at the Ohio and North Carolina sites during the period between April 25, 1987 and December 28, 1987. Results obtained from DI-runoff samples are used to determine the contributions of dry-deposited compounds to the dissolution rates of galvanized steel and an oil-based paint, as determined by the chemical contents of the runoff. In this preliminary analysis, dissolution rates are discussed in terms of relationships between cationic and anionic concentrations in the aqueous-runoff samples and between airborne gas and particulate concentrations and the ionic contents of the runoff. Possible neutralization of dry-deposited acid gases by coarse alkaline particles is also discussed.

EXPERIMENTAL

Covering/spray systems were installed at ground level on the campus of Research Triangle Institute in Research Triangle Park, NC, and on the roof of a two-story building occupied by the North Ohio Valley Air Authority in Steubenville, OH. Each system consists of moveable and stationary racks, a shelter, moisture-sensing information, and a DI-spray system. A schematic of the North Carolina system is shown in Fig. 1. Brief descriptions of the operation of the system and the associated chemical analyses follow; more detailed descriptions have been reported previously (4,5).

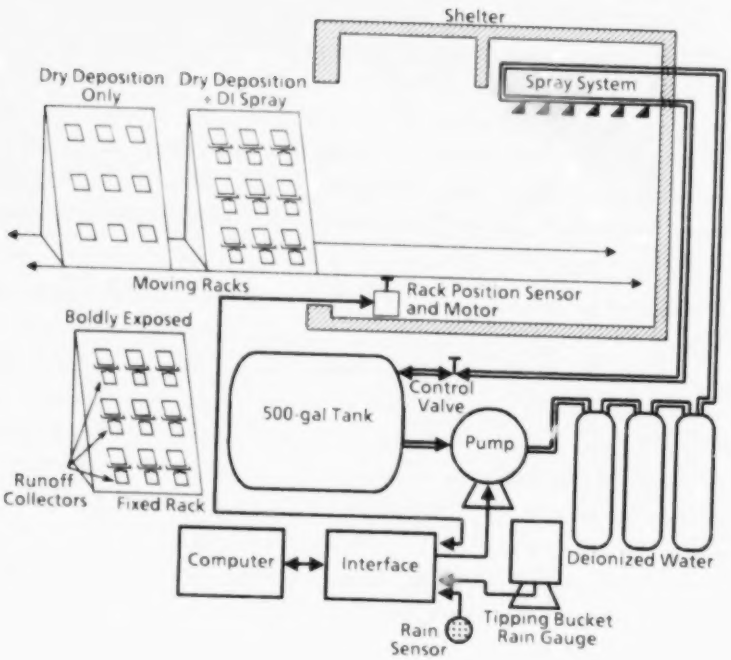

FIG. 1. Schematic of North Carolina Covering/Spray System.

At the onset of precipitation, the moveable racks are automatically brought under the shelter to avoid ambient precipitation. The racks remain inside as long as the moisture sensor is wet. Once the sensor dries, the racks are returned to the ambient-exposure condition. The operation of the DI-spray system at the Ohio site differs from that at the North Carolina site. The North Carolina system is computer-controlled and the test panels, located under the sheltered spray system, are automatically sprayed for a fixed time period ~50 sec for each 0.13 cm of ambient precipitation that accumulates in the exposed tipping bucket. The DI-spray time was selected to deliver to the sheltered panels the approximate volume equivalent to 0.13 cm of precipitation. At the Ohio site, the panels are sprayed with DI after the precipitation event, usually within 18 h.

At each site, runoff collectors, consisting of PVC troughs connected to 1-L polyethylene collection bottles, are located at some of the test-panel positions. Runoff samples are collected on an event basis and detailed chemical analyses are conducted on each sample. The North Carolina samples are analyzed within 24 h of completion of the event, whereas the Ohio samples are shipped by air to Research Triangle Park, NC, where they are analyzed.

The oil-based paint, applied to one side of a 4 × 6 in. stainless steel test panel to an approximate thickness of 1.5 mils, is a high volume, commercial white-exterior paint containing TiO_2 as a pigment, silicates as a filler, alkyd resin as a binder, drying agents, and mineral spirits as solvents. Before being placed in the field, the well-cured paint panels were rinsed with DI. Galvanized-steel test panels were prepared from sheet stock of 20-gauge steel, coated (hot dipped) in Zn with an average coating thickness of 20 μm. Prior to exposure, the virgin steel panels were rinsed with DI and then dried with CH_3OH to remove any moisture. The galvanized steel and paint panels were placed into the field in December 1985, at Research Triangle Park, NC, and in December 1986, at Steubenville, OH.

The results reported here cover the analyses of the DI-spray runoff samples that occurred at both sites between April 25, 1987, and December 28, 1987, a 248-day period. During this time, 25 precipitation events occurred in North Carolina and 28 in Ohio. Each DI-runoff sample was analyzed for Na^+, NH_4^+, K^+, $HCOO^-$, Cl^-, NO_3^-, and $SO_4^=$ by ion chromatography and for Zn and Ca by atomic absorption spectroscopy. In addition, the volume and pH of each sample were determined.

Air quality and meteorological measurements are conducted continuously at each site. Commercial monitors are employed to monitor SO_2, NO_x, and O_3. The following meteorological parameters are measured continuously: wind speed, wind direction, temperature, dew-point, and solar radiation. The air quality and meteorological stations are part of the NAPAP Material Damage Site Network that has been described in detail elsewhere (6).

Ambient particulate concentrations are determined using high-volume and dichotomous sampling devices. Modified Sierra/Andersen dichotomous samplers with 15-μm inlet and 37-mm diameter, ringed Teflon® filters are used to measure fine (<2.5 μm) and coarse (2.5 μm$<d<15.0$ μm) fractions. The sampling system was designed to collect samples every 15 min out of an hour for a week, a procedure developed to avoid plugging the filters. A high-volume sampler is used to measure

TABLE 1
Ambient Gas and Particulate Concentrations [a,b]

	[X] (ng/m³)			
	North Carolina Site		Ohio Site	
Compound	Fine	Coarse	Fine	Coarse
S	2083 (938)	131 (62)	3034 (2294)	302 (534)
Cl	4 (3)	35 (40)	294 (522)	135 (83)
Ca	21 (10)	124 (55)	111 (87)	713 (559)
Na	55 (48)	205 (154)	122 (117)	184 (183)
K	59 (31)	107 (33)	226 (149)	113 (67)
SO_2[c]	2 (2)		22 (32)	
NO_x[c]	23 (25)		44 (40)	
O_3[c]	28 (23)		18 (18)	

[a] Numbers in parenthesis are standard deviations.
[b] Particulate concentrations are weekly averages.
[c] Gas concentrations are hourly averages and are in parts-per-billion.

the total gravimetric particulate concentration. In addition to determining the mass concentrations for the two size fractions, the dichotomous sampler filters are analyzed for chemical composition by X-ray fluorescence. Only the concentrations of particulate Cl, K, Na, and Ca are reported here. Other details of the particle sampling and analysis methods have been published elsewhere (7).

RESULTS

Averages and standard deviations of the ambient hourly averages of gas-phase concentrations and weekly averages of particulate concentrations are presented in Table 1. The average SO_2 value for the Ohio site was 22 ppb, 11 times the value found in North Carolina. In each case, the standard deviation was on the order of the average value. The North Carolina SO_2 levels were low, with 28% of the values less than 1 ppb. Because of these rather small ambient levels, there is some question regarding the accuracy and precision of the measurements; therefore the average value of 2 ppb should be used only as an estimate. The Ohio NO_x values

were about twice those found at the North Carolina site; however, the average O_3 level of 29 ppb in North Carolina is 60% higher than the average in Ohio. This latter result suggests that there was more photochemical activity at the North Carolina site. Although there were differences between the NO_X and O_3 levels, the significant difference between the gas phase species at the sites was the SO_2 level. This suggests that with respect to SO_2-induced reactions, there should have been a substantial difference between the damage occurring at the two sites.

The high-volume particulate concentrations were 32 and 70 $\mu g/m^3$ for the North Carolina and Ohio sites, respectively. At each site, over 90% of the particulate sulfur was found in the fine mode, where, in general, much of the sulfur is associated with acidic-aerosol species. Substantial site differences were found for the particulate Cl, Na, and K, particularly in the fine mode. Elevated levels at the Ohio site may have arisen from combustion particles from local point sources, such as stacks at steel mills located along the Ohio River, and emissions from unpaved surfaces. Coarse Ca concentrations in Ohio were 5.8 times the North Carolina values. The presence of large concentrations of Ca, some of which are expected to be alkaline, raises the possibility that some of the dry-deposited acid gases may have been neutralized by dry-deposited basic particles, a phenomenon similar to that occurring during neutralization of precipitation acids by wind-blown crustal basic aerosols (8).

To analyze the runoff results, it is convenient to define runoff concentrations and runoff rates to parameterize the amounts and rates of compounds depositing to and leaching out of exposed surfaces. The runoff concentration of compound X for rain event j is given by

$$C_j = \frac{[X]_j V_j}{A}$$

where $[X]_j$ and V_j are the molar concentration and volume of runoff, respectively, for the jth event and A is the area of one side of a test panel (155 cm^2). The accumulated runoff concentration, the sum of the runoff concentrations, is expressed as follows.

$$C^{(N)} = \sum_{j=1}^{N} C_j \tag{2}$$

The average runoff rate spanning the entire exposure period is given by

$$R = \frac{C^{(N)}}{t} \tag{3}$$

TABLE 2
Average DI-Spray Runoff Results

Site	Sample	R (nmol/cm²·day)								
		$HCOO^-$	Cl^-	NO_3^-	$SO_4^=$	Na^+	K^+	H^+	Ca	Zn
NC	Galvanized Steel	1.17	1.04	0.60	2.63	0.21	0.23	0.12	0.38	5.34
NC	Paint	0.44	0.37	0.57	0.32	0.15	0.17	0.52	0.36	—*
OH	Galvanized Steel	0.36	2.90	0.62	13.99	0.41	0.47	0.09	7.29	10.05
OH	Paint	0.50	2.43	1.62	7.16	0.49	0.56	0.26	8.35	—*

* Not measured.

where M is the total number of spray events and t, the exposure time, equals 248 days.

The chemical composition of the DI-runoff samples includes only those compounds soluble in dilute solutions of carbonic acid since it is likely that DI, either as spray droplets or as a thin film or droplet on the surface readily equilibrates with atmospheric CO_2 to produce a pH of 5.6. Although many Cl^-, NO_3^-, and $SO_4^=$ salts are soluble under this condition, when utilizing runoff results the possibility must always be considered that gases, particulates, and ions may be irreversibly absorbed by both paint and corrosion films, and only under certain circumstances can runoff concentrations be equated to atmospheric depositions.

Average DI-spray runoff rates are presented in Table 2, and accumulated runoff concentrations are shown in Figs. 2 through 5. Ohio $SO_4^=$ runoff rates, resulting from the dry deposition of particulate $SO_4^=$ and the uptake of SO_2 into films of moisture followed by oxidation, were substantially higher for both the paint and galvanized steel samples than the North Carolina values. The ratios of Ohio to North Carolina $SO_4^=$ runoff rates were 22 and 5 for the paint and galvanized steel samples, respectively. Similar NO_3^- runoff rates were found for samples at both sites with the exception of the Ohio paint-runoff rate that was approximately 2.5 times the value of the other samples. The presence of NO_3^- is due likely to uptake of gaseous HNO_3 and particulate NO_3^- and possibly the absorption of NO_2 into thin films followed by oxidation to NO_3^-. $HCOO^-$ was found in the samples at both sites. The source of runoff $HCOO^-$ has not been established and may depend on the

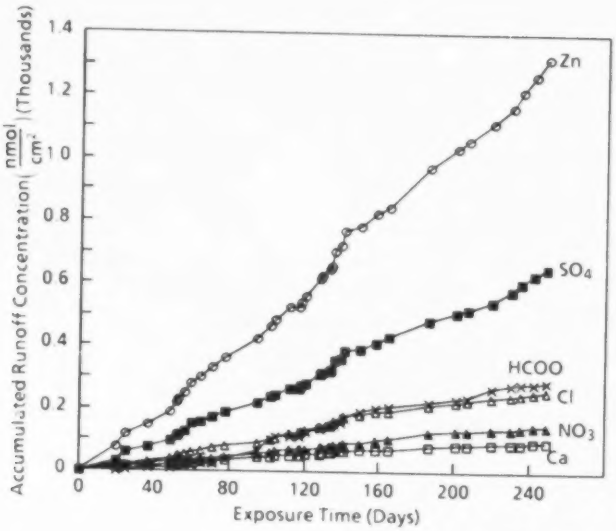

FIG. 2. North Carolina Galvanized Steel Accumulated Runoff Concentrations as a Function of Time.

chemical composition of the material surface. Laboratory studies suggest that HCHO is oxidized to $HCOO^-$ in aqueous films on galvanized steel surfaces (9). HCOOH, a known product of oxidation of polymers, might be expected to be in paint-runoff samples. Another potential source of $HCOO^-$ is dry deposition of HCOOH.

The elevated levels of runoff Cl^- in Ohio were consistent with the higher concentrations of particulate Cl. The same situation was found for Na and K, where both particulate and runoff concentrations were higher in Ohio than at the North Carolina site. With the exception of Cl depositions in North Carolina, the depositions of Cl, Na, and K appear to be independent of surface composition.

Dissolution of galvanized-steel corrosion products generated substantial amounts of Zn in the runoff samples. The average Zn runoff rate at the Ohio site was 1.9 times the North Carolina value, a somewhat surprising result since ambient SO_2 levels differed by an order of magnitude and previous studies have shown a

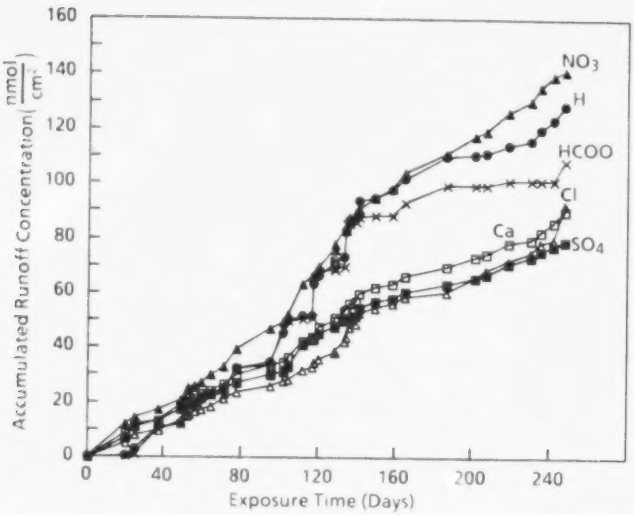

FIG. 3. North Carolina Paint Accumulated Runoff Concentrations as a Function of Exposure Time.

1:1 relationship between SO_2 deposited and Zn dissolved (10). As expected from the differences in particulate Ca levels, significantly larger amounts of Ca were found in Ohio runoff samples than those obtained at the North Carolina site. The ratios of Ohio to North Carolina Ca-runoff rates for the paint and galvanized steel samples were 23 and 19, respectively. If present in the form of a basic salt such as $CaCO_3$, a known crustal component, the dry-deposited Ca compounds could have provided some measure of protection for the Ohio samples by neutralizing some of the depositing acid gases.

To utilize the runoff results fully, all the important ions in the runoff samples must be detected. Some indication of the completeness of the analyses is provided by the charge balance of the runoff results (Table 3). Charge balances for the galvanized-steel runoff results showed an excess of cations at each site. Such unequalities have been found in a previous study, where the discrepancy was

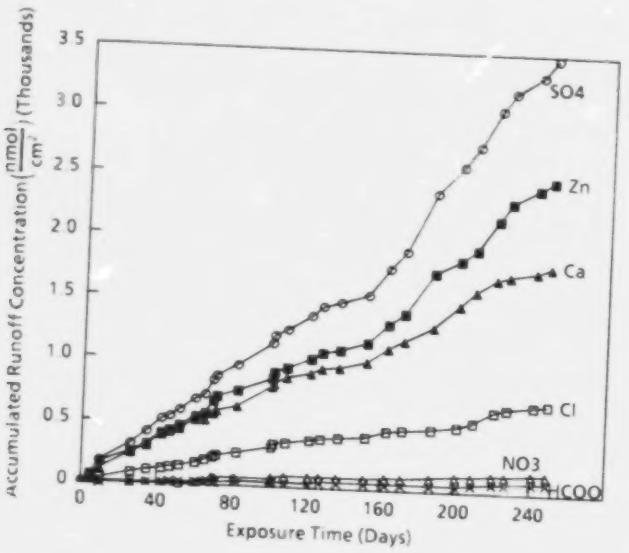

FIG. 4. Ohio Galvanized Steel Accumulated Runoff Concentrations as a Function of Exposure Time.

resolved by postulating the presence of HCO_3^-, an anion expected to be present from dissolution of galvanized steel corrosion products such as $ZnCO_3$ (5). This product is formed by electrochemical Zn reactions followed by reaction with atmospheric CO_2. The Ohio paint-charge balance was good; whereas there appeared to be an excess of anions over cations for paint-runoff results in North Carolina. The discrepancy may have arisen from the accumulation of small errors in the individual event samples or from the presence of cations not analyzed for such as Mg^{++}.

DISCUSSION

Determining the impact of dry deposition of acid gases and particulates on dissolution of surface compounds requires unraveling the relationships between

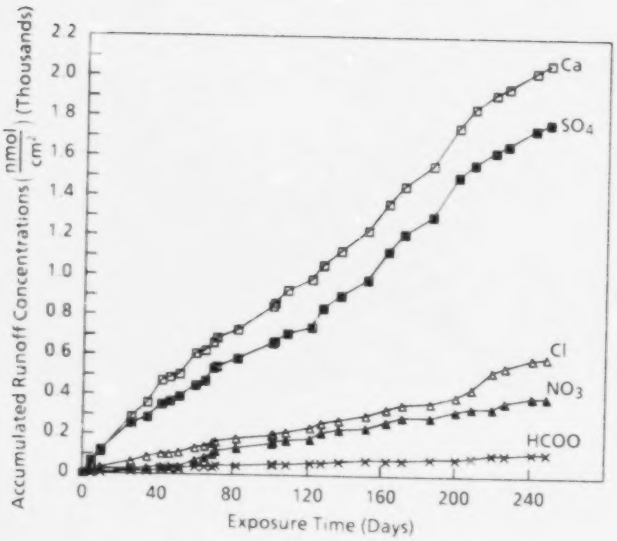

FIG. 5. Ohio Paint Steel Accumulated Runoff Data as a Function of Exposure Time.

TABLE 3
DI-Spray Charge Balance Results [a]

Site	Sample	C+	C-	C+/C-
North Carolina	Galvanized Steel	12.00	8.07	1.49
North Carolina	Paint	1.20	2.02	0.59
Ohio	Galvanized Steel	35.65	31.86	1.12
Ohio	Paint	18.01	18.87	0.95

[a] $C+ = R(Na^+) + R(K^+) + R(H^+) + 2R(Ca) + 2R(Zn)$
$C- = R(HCOO^-) + R(Cl^-) + R(NO_3^-) + 2R(SO_4^{2-})$

concentrations of airborne gas and aerosol compounds and runoff levels of ions such as NO_3^- and $SO_4^=$ and the relationships between these anionic concentrations and the levels of dissolved cations such as Zn^{++} in the case of galvanized steel. In general, surface reactivity will depend upon both the composition of the exposed materials and the salts dry-deposited to the surface.

The dissolution of galvanized steel corrosion products at the Ohio site appears to have been dominated by compounds that form $SO_4^=$, with NO_3^- and $HCOO^-$ playing relatively minor roles. Although it is difficult to partition the contributions of particulate $SO_4^=$ and gas-phase SO_2 to the total $SO_4^=$ runoff rates, it is likely that, due to the rather high levels of SO_2 in Ohio, a significant portion of the galvanized steel $SO_4^=$ resulted from dry deposition of SO_2. At both sites, the largest contributing factor to the dissolution of the Zn corrosion products was apparently SO_2. However, the contributions of NO_3^- and $HCOO^-$ relative to $SO_4^=$ were larger in North Carolina than in Ohio.

The amount of Zn dissolved by SO_2 is affected by the ambient SO_2 level, the presence of moisture, the chemical reactivity of the material, and, in principle, the amount and reactivity of dry-deposited particulates. A variety of studies have shown that the uptake of SO_2 to reactive surfaces is a function of relative humidity (11). Under very dry conditions, SO_2 will deposit and saturate a surface (10). At higher relative humidities, depending on the deliquescent properties of the material as well as those of dry-deposited compounds, aqueous layers will form. For galvanized steel, the relative humidities required for moisture formation may be a function of the exposure history, since recent studies suggest that the time a metal surface is wet is determined by the composition of the corrosion products, which itself is a function of time (12,13).

In the presence of moisture, SO_2 will be absorbed and undergo a series of reversible reactions,

$$SO_2 + H_2O \leftrightarrows SO_2 \cdot H_2O \qquad \text{R1}$$

$$SO_2 \cdot H_2O \leftrightarrows H^+ + \cdot HSO_3^- \qquad \text{R2}$$

$$HSO_3^- \leftrightarrows H^+ + SO_3^= \qquad \text{R3}$$

resulting in acidification of the film. As the H^+ concentration increases, the back reactions become more important and equilibrium is eventually reached. The equilibrium is altered by reactions that irreversibly remove the aqueous reaction products H^+ and/or the S(IV) compounds $SO_2 \cdot H_2O$, HSO_3^-, and $SO_3^=$. Examples of such reactions include removal of H^+ electrochemically, H^+ reaction with alkaline compounds via ion exchange or chemical dissolution, and oxidation of dissolved S(IV) compounds. Under acidic conditions it is generally believed that dissolved H_2O_2 is the major oxidant that converts S(IV) compounds to $SO_4^=$, but for damage to materials, it is more likely that alkaline conditions exist and other oxidation mechanisms favored under basic conditions, such as reactions with dissolved O_3 or O_2, may be important (14). Independent of the specific mechanism that shifts the equilibrium to the right, such reactions will cause more SO_2 to be absorbed, providing a coupling between the rate of deposition and reactions on the surface. Thus, in the absence of oxidants, the amount of SO_2 deposited to an alkaline surface, such as a galvanized steel panel or a surface covered by dry-deposited basic particles, will be greater than to a relatively inert surface, for instance a virgin-paint film containing no alkaline compounds.

The ratio of the DI spray Zn to $SO_4^=$ runoff rate was 0.72, differing from the North Carolina results where the ratio was 2.03 and from a recent galvanized steel SO_2 laboratory exposure study where a 1:1 relationship was found between Zn dissolved and SO_2 deposited (10). In the laboratory study, $SO_4^=$ dominated the composition of the dissolved S ions and thus the 1:1 relationship was a manifestation of simple charge neutrality.

The presence of large amounts of Ca in the Ohio galvanized-steel runoff samples is consistent with the ratio of Zn to $SO_4^=$ being less than one. A substantial amount of the runoff $SO_4^=$ could have arisen from the dissolution of $CaSO_4$. Due to the large amounts of Ca present in the coarse fraction of the Ohio site particulates and the expected alkaline nature of such particles (15), it is possible that at least some of the $CaSO_4$ was generated by absorption of SO_2 onto moist $CaCO_3$ particles followed by oxidation to $SO_4^=$. In terms of chemical dissolution, the reactions of dissolved acid gases are similar for $CaCO_3$ and the galvanized steel conversion product, $ZnCO_3$. In the presence of dissolved acids, the following reactions can take place:

$$XCO_3(s) + H_2O \leftrightarrows X^{++} + CO_3^= \qquad \text{R4}$$

$$H^+ + CO_3^= \leftrightarrows HCO_3^- \quad \text{R5}$$

$$H^+ + HCO_3^- \leftrightarrows H_2CO_3 \quad \text{R6}$$

$$H_2CO_3 \leftrightarrows H_2O + CO_2(g) \quad \text{R7}$$

where X could be Ca or Zn, thus demonstrating that acid dissolution can result from both acids generated from the uptake of CO_2, as well as NO_x compounds and SO_2. To determine whether an acid formed on a moist galvanized-steel panel reacts with the substrate, or is neutralized by dry-deposited $CaCO_3$, requires information beyond the Zn and Ca carbonate concentrations and reaction rate constants for reactions R4-R7, since the dry deposited $CaCO_3$ will likely form a layer over the corrosion products. Thus, the system is not spatially homogenous. The analysis of the system is complicated further by the potential electrochemical reactions involving Zn compounds. Although an alternative explanation for the presence of $CaSO_4$ in the Ohio galvanized-steel runoff samples is simple dry deposition of particulate $CaSO_4$, the result that the coarse Ca to S molar ratio in Ohio was 1.9, is consistent with some of the Ca being present in the form of basic Ca particles. Consequently, there exists the possibility that substantial neutralization of acid gases took place in Ohio.

The dominant cation in the Ohio paint runoff samples was Ca, with levels similar to that found in the galvanized steel samples. Since the paint contained no Ca, the source of the Ca was again atmospheric deposition. In the absence of alkaline dry-deposited compounds or alkaline compounds in the paint film, the uptake of SO_2 to the film should have been small because of the inert nature of the film. The oil-based paint does not contain reactive basic components such as $CaCO_3$, ZnO, or aluminum oxides. Thus, assuming that the dry-deposited Ca was in the form of a basic Ca compound, the reactivity of the paint film at the Ohio site may have been controlled by particle loading. The presence of large surface concentrations of basic compounds could increase the surface reactivity so that in terms of sensitivity toward acid gases, the paint film resembles a reactive galvanized-steel surface more than an inert surface. As opposed to the situation at the North Carolina site, where the Ca runoff rates were only 5% of those in Ohio and the $SO_4^=$ paint runoff rate was only 12% of the corresponding value for galvanized steel, the amount of $SO_4^=$ found in the Ohio paint runoff was 51% of the value found for galvanized steel.

The North Carolina runoff results are more complicated than those in Ohio because the anionic contents of the runoff samples were not completely dominated by $SO_4^=$. For galvanized steel, the $HCOO^-$ runoff rate was larger than the rate for NO_3^- and was 44% of the $SO_4^=$ rate. Both the paint NO_3^- and $HCOO^-$ runoff rates were greater than the corresponding value for $SO_4^=$. These results suggest that there are likely to be areas of the United States where analyses of material damage may require including the effects of NO_X compounds, HCHO, and organic acids. However, since SO_2 levels tend to be greater than the aforementioned compounds, it may be that in those areas where significant amounts of damage by dry-deposition processes occur, the dominant compound is SO_2.

The ratio of Zn to $SO_4^=$ for galvanized steel at the North Carolina site was 2.03. This result is consistent with the presence of compounds other than $SO_4^=$ that can dissolve Zn corrosion products and the absence of $CaSO_4$. In addition to contributions by $HCOO^-$, NO_3^-, and $SO_4^=$, it is likely that a substantial amount of the dissolved Zn came from dissolution of corrosion products by H_2CO_3 generated in the DI spray by acidification due to atmospheric CO_2 (R4-R7). The reported solubility of $ZnCO_3$ in aqueous solutions in the presence of 320 ppm CO_2 is 80 μM (16). However, this concentration is only reached if there is sufficient time for the system to reach equilibrium. Determining the impact of uptake of CO_2 at the two sites is complicated further by the different methods used to spray the samples; possibly generating different droplet residence times. At the North Carolina site, the panels were sprayed automatically after each 0.13 cm of ambient precipitation deposited, whereas in OH, the panels were sprayed only at the completion of the event.

The lack of reactivity of the paint panel at the North Carolina site is demonstrated by a galvanzied steel to paint panel $SO_4^=$ runoff rate ratio of 8.2, and the most abundant paint runoff cation being H^+. The apparent lack of reactivity of the paint film toward acids suggests that if pollution increases the weathering rates of paints containing no alkaline components, the degradation is either initiated by a photodegradation process and/or uptake and subsequent reaction of gas-phase pollutants soluble in the polymer. Such reactions could initiate microscopic changes in the paint film, such as increases in crosslinking or chain scission, that ultimately could lead to microscopic damage, such as cracking or the destruction of the protective nature of the film leading to exposure of the substrate to the environment.

Comparison of the Zn runoff rates at the two sites provides a measure of the relative performance of galvanized steel due to dry-deposition processes. Although it is difficult to compare the possible effects of the acidification of the DI-spray droplets on the dissolution rates of the corrosion products, this preliminary analysis of the runoff rates suggests that, at least at these two sites, the Zn dissolution rates are not directly proportional to the ambient SO_2 level. Although the average SO_2 level at the Ohio site was 11 times the North Carolina value, the Ohio Zn dissolution rate was only approximately twice the corresponding rate in North Carolina. One possible explanation for this discrepancy is neutralization of depositing acids by dry-deposited alkaline particles.

Clearly, further analysis of the runoff data and ambient concentrations is required. Calculations should be conducted to determine whether the runoff rates of Ca, Na, K^+, Cl^-, NO_3^-, $SO_4^=$, etc., are consistent with the expected depositions of their airborne gas and particulate precursors. In addition, the analysis should be extended to include the results of the ambient runoff data. Additional measurements should be conducted to determine in an unambiguous way the extent to which the source of $CaSO_4$ is neutralization of SO_2 by dry deposited $CaCO_3$. Such investigations are presently underway and will be the subject of future publications.

DISCLAIMER

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